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Emerging Energy Efficiency and Carbon Dioxide Emissions-Reduction Technologies for Industrial Production of Aluminum

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Abstract

Aluminum production is among the most energy-intensive industries and accounts for one percent of total global carbon dioxide (CO_2) emissions. The ongoing increase in world aluminum demand means that this industry's energy use and CO_2 emissions will continue to grow. There is significant incentive to develop, commercialize and adopt emerging energy efficiency and CO_2 emissions-reduction technologies for aluminium production. Although studies from around the world have identified a wide range of energy efficiency technologies applicable to the aluminum industry that have already been commercialized, information is limited and/or scattered regarding emerging or advanced energy efficiency and low-carbon technologies that are not yet commercialized. This report consolidates available information on 10 emerging aluminum industry technologies, with the intent of providing a well-structured database of information on these technologies for engineers, researchers, investors, aluminum companies, policy makers, university students, and other interested parties. For each technology included, we provide information on energy savings and environmental and other benefits, costs, and commercialization status; we also identify references for more information.

Contents

Acronyms

ACD	anode-cathode distance
ACEEE	American Council for an Energy-Efficient Economy
ARP	Advanced Reactor Process
ARPA-E	Advanced Research Projects Agency – Energy
CCS	carbon capture and storage
CO	carbon monoxide
CO_2	carbon dioxide
GJ	gigajoules
IEA	International Energy Agency
kg	kilogram
kWh	kilowatt-hour
LIBS	laser induced breakdown spectroscopy
MEA	monoethanolamine
MHD	magnetohydrodynamic
Mt	million metric tonnes
PFC	perfluorocarbon
SPL	spent potliner
TiB_2	titanium diboride
ton	metric ton
U.S. DOE	U.S. Department of Energy
V	volts

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1. Introduction

Aluminum production is one of the most energy-intensive industrial processes worldwide. Although about a third of global aluminum production uses electricity from hydropower sources, the increasing use of coal as the primary fuel for electricity for aluminum production in many countries means that aluminum production is still a significant source of carbon dioxide (CO_2) and greenhouse gas emissions. According to the International Energy Agency (IEA), the aluminum industry accounts for about 1% of global CO_2 emissions (IEA 2012).

Annual world aluminum demand is expected to increase two- to three-fold by 2050. The bulk of growth in consumption of aluminum will take place in China, India, the Middle East, and other developing countries, where consumption is expected to nearly quadruple by 2025 (Menzie et al. 2010). To meet this increased demand, production is projected to grow from approximately 51 million tonnes (Mt) of primary aluminum in 2014 to 89-122 Mt in 2050 (IEA 2012). This increase in aluminum consumption and production will drive significant growth in the industry's absolute energy use and CO_2 emissions.

Studies have documented the potential for the global aluminum industry to save energy by adopting commercially available energy efficiency technologies and measures (IEA 2012, Worrell et al. 2007). However, in view of the projected continuing increase in absolute aluminium production, future reductions (e.g., by 2030 or 2050) in absolute energy use and CO_2 emissions will require innovation beyond technologies that are available today. New developments will likely include different processes and materials as well as technologies that can economically capture and store the industry's CO_2 emissions. Deployment of these new technologies in the market will be critical to the industry's climate change mitigation strategies for the mid- and long-term. It should be noted that technology adoption in regions around the world is driven by economic viability, raw materials availability, energy type used and energy cost as well as regulatory regime.

Many studies from around the world have identified sector-specific (e.g., U.S. DOE 2003, Evans and Kvande 2008) and cross-cutting (e.g., IEA 2012, Worrell et al. 2007, U.S. DOE/AMO 2012) energy efficiency technologies for the aluminum industry that are already commercially available. However, information on emerging or advanced energy efficiency and low-carbon technologies for the industry is highly limited, decentralized, and not easily accessible. This report consolidates the publicly available information on emerging technologies for the aluminum industry to assist engineers, researchers, investors, aluminum companies, policy makers, and other interested parties.

The information presented in this report is collected from publically available sources and covers the main emerging energy efficiency and low-carbon technologies for the aluminum industry; however, the list of emerging technologies addressed is not exhaustive.

The report uses a uniform structure to present information about each of the 10 technologies covered. First, we describe the technology, including background, barriers, and case studies if available. Next, we present the energy, environmental, and other benefits of the technology as well as cost information if available. For most technologies, we include a block diagram or picture. Finally, we identify the commercialization status of each technology as well as resources for further information. The commercialization status of each technology is as of the writing of this report and uses the following categories:

- Research stage: The technology has been studied, but no prototype has been developed.
- Development stage: The technology is being studied in the laboratory, and a prototype has been developed.
- Pilot stage: The technology is being tested at an industrial-scale pilot plant.
- Demonstration stage: The technology is being demonstrated and tested at the industrial scale in more than one plant but has not yet been commercially proven.
- Commercial with very low adoption rate stage: The technology is proven and is being commercialized but has a very small market share.

Table 1 lists the 10 technologies covered in this report, the section of the report in which each technology is discussed, and the technology's commercialization status.

The purpose of this report is solely informational. Many emerging technologies are proprietary and/or the manufacturers who are developing a new technology are the primary sources of information about it. Thus, in some cases, we identify a company that is the source of a technology so that readers can obtain more information about the company and product.

Because the nature of emerging technologies is continual and often rapid change, the information presented in this report is also subject to change. If readers are aware of a new technology that is not presented in this report or have updated information about a technology that is described in this report, please contact the authors.[1]

Table 1. Emerging energy efficiency and CO_2 emissions-reduction technologies for the aluminum industry

Report Section/Technology Name	Commercialization status
3.1. Emerging Electrode Technologies	
3.1.1. Inert Anodes	Demonstration stage
3.1.2. Wetted Cathodes	Demonstration stage
3.1.3. Multipolar Cells	Development stage
3.1.4. Novel Physical Design for Anodes	Commercial with low adoption stage
3.2. Alternative Reduction Technologies	
3.2.1. Carbothermic Reduction	Pilot stage
3.2.2. Kaolinite Reduction	Research stage
3.3. Emerging Low-Temperature Reduction Technologies	
3.3.1. Ionic Liquids	Development stage
3.4. Carbon Capture and Storage Technologies for the Aluminum Industry	
3.4.1. Carbon Capture Using Absorption Technologies	Development stage
3.5. Emerging Aluminum Recycling Technologies	
3.5.1. Novel Physical Recycling Techniques	Demonstration stage
3.5.2. Aluminum Mini Mills	Pilot stage

2. Description of Aluminum Production

Aluminum ore (bauxite) is first processed into alumina via the Bayer process. Alumina is then reduced to aluminum via the Hall-Héroult process. The Hall-Héroult process is briefly explained in the section below, following a brief summary of where aluminum is produced.

2.1. Global Trends in Aluminum Production

Bauxite is a highly abundant ore, often mined and processed into alumina in the same location, before being transported to an aluminum smelter (often outside of the bauxite-producing country). Some countries are major bauxite miners and alumina producers by virtue of having highly concentrated bauxite deposits (such as Jamaica and Guinea). Others, like Australia, capitalize on their advanced technologies and vast land area to produce large amounts of bauxite and alumina. China and Australia are the world's top bauxite and alumina producers, while China is also the world's top aluminum producer (USGS 2015). China produces nearly eight times as much aluminum as the world's second largest aluminum producer, Russia.

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Globally, aluminum smelters are located in areas where electricity is inexpensive and abundant, due to the massive amounts of electricity required to produce aluminum. Over time, this has led to a decrease in aluminum smelters in the United States, Japan, Brazil and some European countries, and an increase in countries like China and India with low electricity costs. Aluminum production in China has skyrocketed since 2003, increasing five-fold in just ten years. Since 2010, a number of Middle Eastern countries have begun significant aluminum production due to abundant energy there. In addition, while aluminum production was once dominated by a handful of multinational companies, today, a larger and more diverse group of companies produce aluminum, many of them state-owned enterprises in developing countries (Nappi 2013).

2.2. Aluminum Production Process and Energy Use

Figure 1 is a simplified diagram. The following subsections describe the main production steps of aluminum, from mine to metal.

1. Bauxite Mining	**2. Bayer Process (Alumina)**
Strip mining	Digestion
Initial processing	Clarification
Transport	Precipitation
	Calcination
	Transport

3. Hall-Heroult Process (Aluminum)

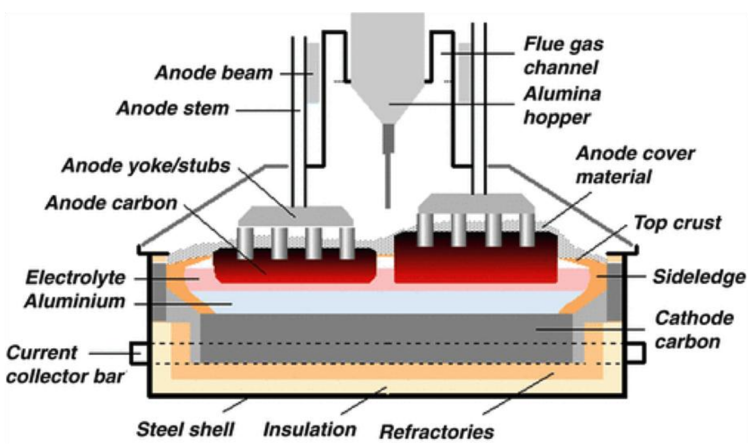


Figure 1. Diagram of the major steps of primary aluminum production (image source: Haarberg 2014)

2.2.1. Bauxite Production

Aluminum is abundant in the earth's crust, but since the metal is highly reactive, it typically exists in its oxidized form. The term 'bauxite' refers to ores that contain a high (over 35%) concentration of aluminum hydroxide minerals. The three main types of bauxite are gibbsite, böhmite and diaspore. Böhmite and diaspore have a different crystalline structure and hydrate content, and require higher temperatures and pressures than gibbsite for processing (Tabereaux and Peterson 2013). Bauxite mining begins with mechanical removal of the overburden layer covering the bauxite, which ranges from 2-20 meters in depth (Wagner et al. 2010). Since bauxite deposits tend to be soft and earthy, high-energy operations like drilling and blasting are not used as intensively as for some other ores. In addition, bauxite mines are often open-pit mines, eliminating the need for energy-intensive ventilation and de-watering processes. Loading and hauling is the most energy-intensive process in bauxite production, usually carried out by diesel-powered trucks and excavators (Norgate and Haque 2010). Bauxite requires minimal processing before moving to an alumina production plant – bauxite may be crushed, ground, and beneficiated, with beneficiation used mainly to remove clay. This can be achieved by washing, wet screening, cycloning, or sorting the bauxite. The estimated primary energy demand for producing bauxite is about 278 kWh/ton (1 GJ/ton) (The Aluminum Association 2013).

2.2.2. Alumina Production

The subsections below describe the Bayer Process, which refines bauxite into alumina and is the main alumina production process used throughout the world. Overall, the Bayer process is estimated to require about 4028 kWh/ton (14.5 GJ/ton) of primary energy per ton of alumina produced on average, or 8056 kWh/ton (29 GJ/ton) per ton of aluminum (International Aluminium Institute 2012). As a rule of thumb, about two tons of bauxite are required to produce one ton of alumina, and two tons of alumina are require to produce one ton of aluminum.

Digestion

Mined bauxite is first washed and crushed in order to increase the surface area available for reaction. Some bauxite goes through desilication to remove impurities. The bauxite is then dissolved in a series of high-pressure digesters at either low temperatures (~100 °C) or high temperatures (~250 °C) with the addition of a caustic soda solution. Low temperature digestion of gibbsite bauxite requires 2083-3333 kWh/ton (7.5-12 GJ/ton), while high temperature digestion of böhmite or diaspore bauxite requires 3055-5000 kWh/ton (11-18 GJ/ton) (Tabereaux and Peterson 2013).

Clarification and Precipitation

Clarification separates solid bauxite residue ('red mud') from the desired sodium aluminate. The sediment sinks to the bottom of settling tanks, and is then removed and washed. The sodium aluminate solution is then filtered further. Cooling the sodium aluminate solution and adding mineral crystals leads to precipitation of hydrated alumina crystals ($Al(OH)_3$). Cyclones or gravity classification tanks separate coarse crystals out for calcination.

Calcination

These coarse crystals are baked in calciners at high temperature (900-1300 °C) to remove water of hydration and produce metallurgical-grade-purity alumina (Al_2O_3). Alumina calciners use a range of technologies, including gas suspension calciners (GSC), fluidized bed calciners (FBC), and rotary kilns. The final alumina product is then transported to aluminum smelters. The aluminum industry is discontinuing rotary kilns in favor of stationary calciners (GSC and FBC types), which consume about 33% less energy (3.0 GJ/ton alumina compared with 4.5 GJ/ton alumina). The calcination step requires about 25% of the total energy in the Bayer Process.

2.2.3. Aluminum Production

The subsections below describe the Hall- Héroult process of aluminum smelting, and outline the major determinants of its energy use and environmental impact.

The Hall-Héroult Process

The Hall-Héroult process for electrochemical reduction of alumina to aluminum was first patented in 1886, and it is still the main method of aluminum production today. Electrolysis takes place in a Hall-Héroult cell, or pot, which is typically a shallow rectangular steel basin from 9 to 18 meters long depending on amperage, lined with carbon. In order to keep various materials molten, the cells operate at around 950-960 °C. Inside the cells, a molten cryolite (Na_3AlF_6) electrolyte or "bath" serves as the conductor for the electric current running through the carbon anode to the positively charged surface of newly formed molten aluminum on the carbon lining (the cathode). Aluminum fluoride (AlF_3) is added to the solution to maintain optimal chemistry and lower the electrolyte's freezing point. Beneath the carbon lining, steel bars pick up the electric current and take it to the next cell. Long rows of cells are connected in an electrical series (potline), sometimes up to around 400 cells per potline and more than one kilometer long. Automatic feeders continuously add alumina to cells, which dissolves in the molten electrolyte. As the electrical current passes through the solution, the dissolved alumina is split into molten aluminum ions (Al^{3+}) and oxygen ions (O^{2-}). The oxygen consumes the carbon in the anode blocks to form carbon dioxide.

Molten aluminum produced at the cathode surface is regularly removed by siphon from the top of the cell. Electrolysis through the Hall-Héroult process is by far the most energy-intensive step of primary aluminum production, requiring about 13,000 kWh/ton (47 GJ/ton) in best-practice settings-(Worrell et al. 2007).

Although the Hall-Héroult process was first developed over 100 years ago, it is still essentially the only commercialized production route for primary aluminum. The production of secondary aluminum from scrap and recycled aluminum is becoming an increasing source of the metal – in 2011, the amount of remelted and recycled aluminum approximately equaled the amount of primary aluminum produced (Tsesmelis 2013).

Carbon Anode Production

The overall reaction takes place at the bath-metal interface as the reduction of alumina and the oxidation of the carbon anodes, producing pure aluminum and carbon dioxide. This reaction means that over time, the carbon anode is consumed. Consequently, the carbon anodes must be replaced about once a month in most aluminum smelters. There are two types of anodes: Soderberg anodes and pre-baked anodes. Currently, all new aluminum smelters use pre-baked anodes, which are so named because baking them bonds the calcined petroleum coke and coal tar pitch together. Aluminum or copper rods attached to a steel yoke assembly are connected by steel stubs (inserted and secured by molten cast iron) into the anodes to deliver electricity. The anodes are replaced before they are completely consumed. Anode production is itself an energy-intensive process, require about 444 kWh/ton (1.6 GJ/ton) under best-practice conditions (Worrell et al. 2007)

Anode-Cathode Distance

The anode-cathode distance (ACD) is the distance between the electrode surfaces in a given Hall-Heroult cell. It averages around 4-5 cm. The ACD is one of the main determinants of the voltage necessary for the current to pass through the bath and drive electrolysis. Voltage, in turn, determines electrical energy requirements (with a constant amperage cell operation). A lower ACD reduces voltage, but if the electrode surfaces come into contact, the cell will short circuit. Magnetohydrodynamic (MHD) forces in the cell cause the surface of the molten aluminum to deform and in some cases undulate, and the ACD must be wide enough to accommodate this motion.

Operating Temperature

The molten bath chemistry is a major determinant of the temperature at which a Hall-Heroult cell operates (typically 950-960 °C). The temperature affects the electrical resistance of the bath and thus the total cell voltage. A lower cell temperature also reduces the solubility range for alumina, decreasing cell operating efficiency.

Anode Effects

Current Hall-Héroult cells are susceptible to anode effects, which are triggered by depletion of the alumina concentration. When this concentration becomes too low for normal cell operation, an anode effect occurs, characterized by formation of carbon monoxide and perfluorocarbons (PFCs) and smaller amounts of carbon dioxide, the ordinary reaction product. The bottom surface of the anode becomes covered by a gas film, leading to high voltages, typically 30 to 40 V (over usual levels of 3.5-4.5 V). The smaller the anode surface immersed in bath, the higher the anode effect voltage. Anode effects thus lower cell operating efficiency, cause a spike in energy requirements, and evolve potent greenhouse gases.

2.2.4. Casting, Rolling, and Extrusion

The molten aluminum produced from the Hall-Heroult process is typically cast into ingots, which are then transported to foundries and other processing plants to be transformed into alloys or final products. Aluminum foundries may re-melt the ingots to produce desired alloys, which are then cast into the required shapes for consumer or industrial products. The malleability of aluminum metal means it is also well-suited for rolling into thin sheets. Aluminum may also be extruded into its final shape. The products from the mills may be further processed in various ways, such as coating or painting. Casting, rolling, and extrusion mills consume fossil fuels for reheating the aluminum ingots, as well as electricity, leading to indirect greenhouse gas emissions. Best-practice energy intensity for this casting is estimated at 278 kWh/ton (1 GJ/ton) (Worrell et al. 2007), though some finishing processes may require more energy than this.

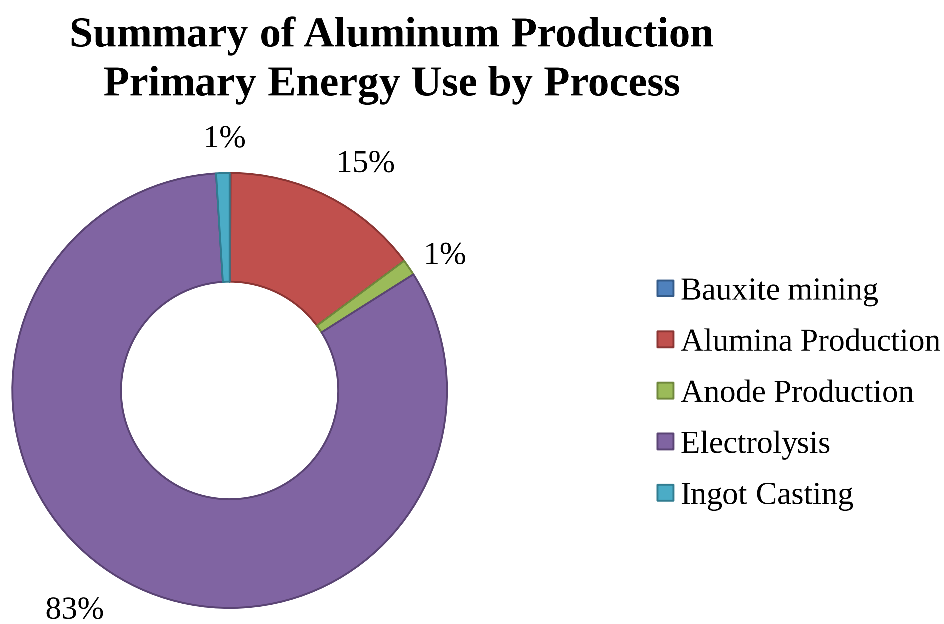


Figure 2: Summary of Aluminum Production Primary Energy Use by Process. Data were from the International Aluminium Institute 2010 Life Cycle Inventory of Primary Aluminium Production. Data presented as shares of primary energy use in kJ per ton of final aluminum produced, using regional production-weighted fuel energy contents.

2.3. CO_2 Impact of Aluminum Production

Aluminum production generates CO_2 emissions as 1) direct process emissions, in which CO_2 is the product of aluminum electrolysis and oxidation of the carbon anode; and 2) indirect emissions from consumption of electricity used for smelting.

For direct process emissions, about 1.6 kg of CO_2 are emitted for every kg of aluminum produced (U.S. DOE 2007). In the case of an anode effect, the cell will evolve PFC gases such as CF_4 and C_2F_6, which are 6,630-11,100 times more potent greenhouse gases than CO_2 (Wong et al. 2015).

Indirect emissions from electricity generation also vary greatly based on fuel type used for generation. For example, coal-fired electricity will generate around 16 kg of CO_2 per kg of aluminum produced, whereas smelters co-located with hydropower plants will generate almost no emissions from electricity.

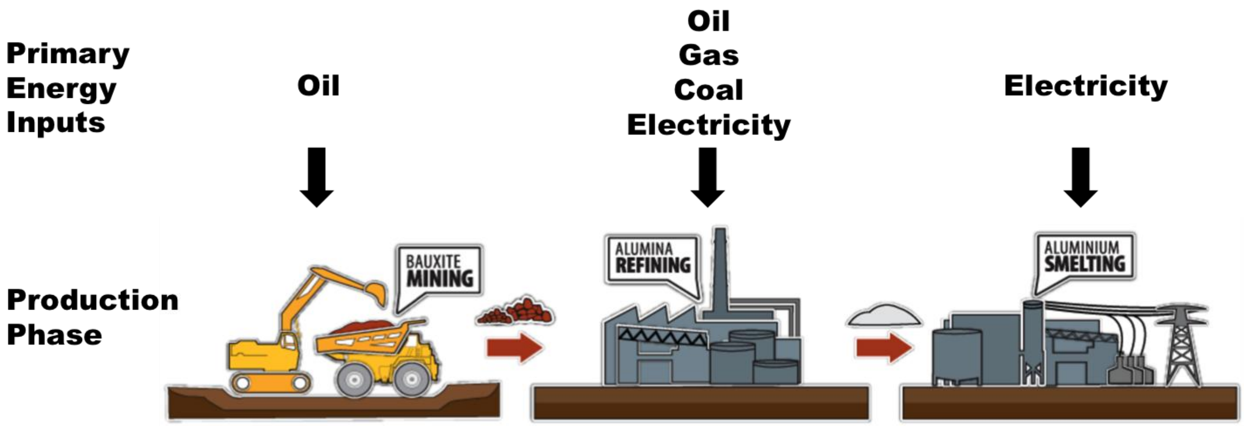


Figure 3: Simplified graphic of primary energy inputs by production phase

3. Emerging Energy Efficiency and CO_2 Emissions Reduction Technologies

The subsections below describe emerging energy efficiency and CO_2 emissions reduction technologies for the aluminum production process. This section focuses primarily on technologies for improving the Hall-Héroult process, also known as the smelting phase of primary aluminum production, which is by far the most energy-intensive phase.

3.1. Emerging Electrode Technologies

Improving electrodes is the main pathway for making the Hall-Héroult process more efficient. Advanced electrode materials can safely reduce the anode-cathode distance, and novel physical designs for electrode placement and orientation can also improve reaction efficiency. Below, emerging technologies for improving electrodes in the Hall-Héroult process are presented.

3.1.1. Inert Anodes

Description:

Inert anodes can significantly improve the Hall-Héroult process for producing aluminum by eliminating the need for regular replacement of the carbon anodes currently used in Hall-Héroult cells. Ideal inert anodes are chemically nonreactive and are not consumed by the electrolysis reaction, and thus could ideally have the same lifetime as the smelting cell (Kvande and Drabløs 2014). Materials that have been considered for inert anodes include metals, ceramics, and cermets, a mix of these two.

In addition to eliminating the energy and material needs for frequently replaced carbon anodes, inert anodes can reduce the ACD in a Hall-Héroult cell, which as described in Section 2 is a major determinant of electricity used by the cell. Inert anodes could be easily installed retrofits in existing cells, with limited changes in smelter infrastructure. In addition, since regular access to the cells to change the anodes would not be necessary, the cells can be sealed more effectively to improve operating efficiency. Alternatively to a retrofit, inert anodes are also easily incorporated into new cell designs that use other technologies described below, such as wetted cathodes and low-temperature baths, all of which can further improve energy and environmental benefits.

A major barrier to designing inert anodes is finding cost-efficient anode materials that do not corrode significantly in the reaction solvent. Corrosion would not only mean that the anodes might have to be replaced more often than desired, but it would also add impurities to the aluminum produced (Kvande and Drabløs 2014).

The company INFINIUM is working on inert anodes sheathed with zirconium oxide (zirconia) tubes. The long-lasting tubes form a barrier between metal produced at the cathode and gas produced at the anode, preventing back-reaction and current leakage, and reducing harmful byproducts. The zirconia tubes would also expand the range of materials that could be used as an anode, possibly even holding liquid metal anode materials (INFINIUM 2013a). INFINIUM has already demonstrated the technology for magnesium, titanium, and rare earth metal production, and with funding for ARPA-E is working on adapting the technology for aluminum production (INFINIUM 2013b).

Rusal is developing inert anode technology both to be used as a retrofit for their current smelters, as well as in new greenfield projects, combined with other design improvements (Evans and Kvande 2008). Pilots were planned to begin in 2015. Alcoa has also piloted inert anode technologies at a multi-pot scale as of 2013, but technical and cost goals have yet to be achieved (AeroWeb 2013).

Energy/Environment/Cost/Other Benefits:
Compared to conventional Hall-Héroult smelting with carbon anodes, inert anodes can have the following benefits:

- Energy savings of 3%-4% within a modified Hall-Héroult cell (U.S. DOE 2007)
- Reducing cost of production and replacement of the consumable carbon anode. Capital costs for inert anodes could be 10%-30% lower than that for conventional anodes (Thonstad 2001, Keniry 2001)
- Eliminating greenhouse gases produced by electrolysis with carbon anodes (CO_2, carbon monoxide, and PFCs) (Kvande and Drabløs 2014). Inert anodes produce oxygen instead. (U.S. DOE 1999)

- Improving occupational health by eliminating the need to regularly replace carbon anodes in the smelting cells (Kvande and Drabløs 2014).
- Improving plant operating efficiency by eliminating anode effects (Kvande and Drabløs 2014)
- For the INFINIUM inert anodes with zirconia tubes, reducing cell energy losses by 60% or more (INFINIUM 2013b)

Block Diagram or Photo:

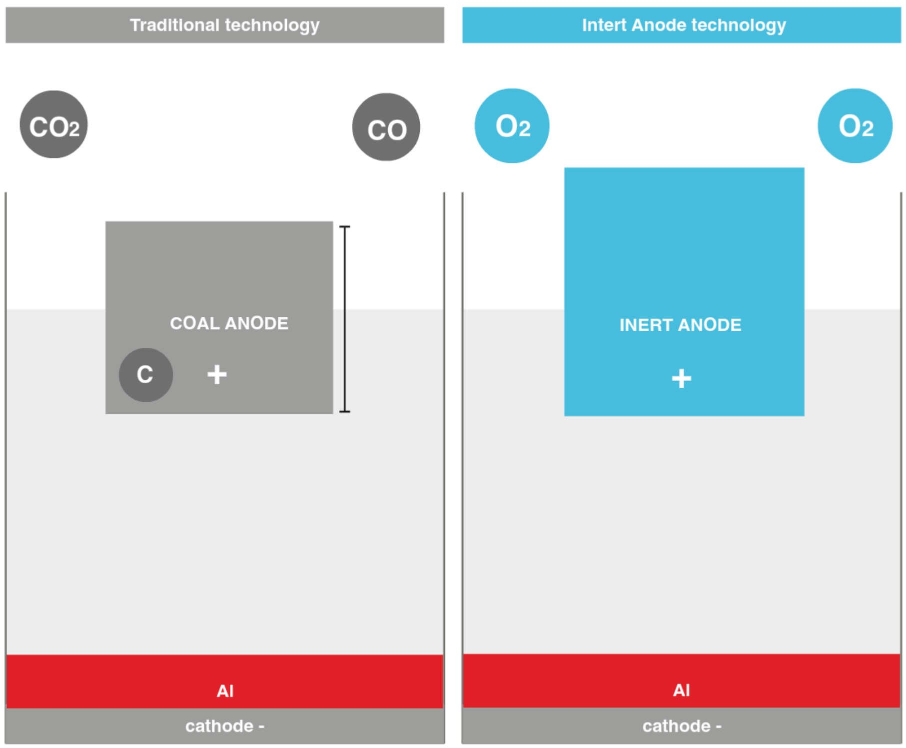


Figure 4: Comparison of a traditional Hall-Héroult cell, which produces carbon dioxide and carbon monoxide and is consumed over time, and a cell with inert anodes, which produces oxygen. Source: Rusal 2014

Commercial Status: Demonstration stage

References for further information: Kvande and Drabløs 2014, Evans and Kvande 2008, U.S. DOE 2007, Keniry 2001, Thonstad 2001, Rusal 2014

3.1.2. Wetted Cathodes

Description:

The cathode in a Hall-Héroult cell is technically the negatively charged surface of the molten aluminum that is being formed by electrolysis, but usually ‘cathode’ refers to the solid carbon material upon which the molten aluminum collects. The molten aluminum is somewhat stable under normal operational conditions, but bringing the anode closer to it causes large waves due to MHD forces (Blais et al, 2013). A stable, wetted cathode would allow the anode to be brought closer without high MHD instability and elevated risk of an anode effect or other problems. ‘Wetting’ refers to improved electrical contact between the molten aluminum and the carbon cathode material (Green 2007). A completely wetted cell lining that was also inert to the cell bath would allow molten aluminum to be drained out of the anode-cathode spacing. This design could withstand a smaller ACD, leading to significant energy savings. Titanium diboride (TiB_2) is a durable, wetted cathode material that can withstand the corrosive and high temperature conditions within a cell. The shape and orientation of the TiB_2 or TiB_2 composite cathodes can also play a large role in how effective they are in mitigating wear and improving the ACD (Bouchard and Tremblay 2013).

Wetted cathodes face several design challenges, namely compensating for complications that arise with a smaller ACD and lower voltage operation. These include lost heat energy and impeded circulation and mixing of the molten bath (Green 2007). Finally, TiB_2 and related composites can be very expensive (Welch 1999).

TiB_2 cathodes were piloted as early as the 1960s by Kaiser Aluminum, however, the materials at the time were unable to withstand the cell environment (Bouchard and Tremblay 2013). Reynolds Aluminum (which was acquired by Alcoa) tested a small pilot cell with wetted cathodes in partnership with the U.S. Department of Energy in the early 2000s (Bruggeman 2002). Recent research has focused on the development of improved TiB_2 composite materials and cathode designs.

Energy/Environment/Cost/Other Benefits:
Compared to conventional Hall-Héroult smelting with carbon cathodes, wettable TiB_2 cathodes can have the following benefits:

- Reducing energy consumption by about 20% by lowering the ACD (Bouchard and Tremblay 2013) (Green 2007).
- Extending cell life by preventing contamination with bath chemicals and lowering the formation of undissolved alumina sludge (Green 2007)
- Reducing the amount of toxic, spent potliner (SPL) waste from carbon cathodes (Green 2007)

Block Diagram or Photo:

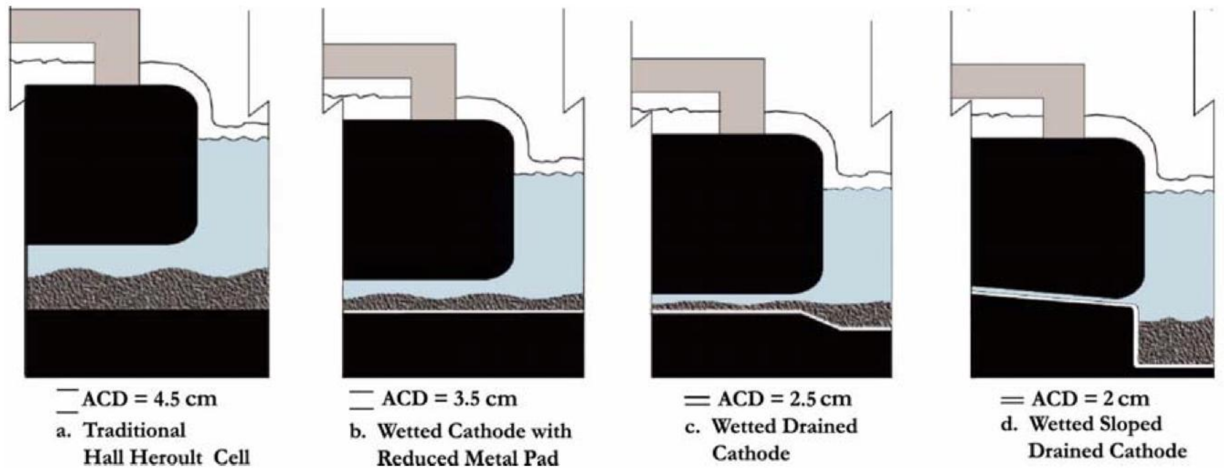


Figure 5. Several possible concepts for wetted cathode and draining cells, compared with a traditional Hall-Héroult cell. Source: U.S. DOE 2007

Commercial Status: Demonstration stage

References for further information: Blais et al. 2013, Bouchard and Tremblay 2013, Green 2007, Welch 1999, Bruggeman 2002, U.S. DOE 2007

3.1.3. Multipolar Cells

Description:

Current Hall-Héroult cells consist of multiple anodes (24 to 48 depending on amperage) with the horizontal bottom surface immersed in a bath and a horizontal cathode surface. This single-pole arrangement is highly capital-intensive. Multipolar cells could greatly increase productivity within a cell by placing multiple electrodes in a single reaction area. Multipolar cells can only work with inert anodes, due to the need for a stable ACD. There are two possible designs for multipolar cells – one would place bipolar electrodes to conduct the current between an anode and cathode; the other would have multiple pairs of anodes and cathodes in the same cell (U.S. DOE 2007). Multipolar cells can produce aluminum at lower temperatures (around 700 °C) and higher current densities than Hall-Héroult cells, in addition to the benefits of inert anodes, which are not consumed and do not evolve harmful gases. Energy efficiency in multipolar cells is achieved by higher electrical conductivity and a lower ACD.

Multipolar cells face materials challenges for anode, cathode, and bath chemistry. In addition, multipolar cells require new configurations for removal of molten aluminum and gas products.

In 1976, Alcoa piloted an aluminum plant with high-efficiency multipolar cells. The pilot successfully demonstrated that multipolar cells could operate more efficiently than current Hall-Héroult cells, but the plant was ultimately closed due to the high cost of operation. The cell used a molten chloride electrolyte and the technology had the additional cost from converting alumina to aluminum chloride. Later, Northwest Aluminum researched multipolar cells with inert anodes and wettable cathodes in a vertical orientation. More recently, the Argonne National Laboratory has been conducting research on multipolar cells (U.S. DOE 2007).

Energy/Environment/Cost/Other Benefits:

- Energy savings of around 40% over current Hall-Héroult cells, in part by operating at lower temperatures and allowing better control of heat loss (U.S. DOE 2007)
- An electrode operating life of nearly three years (versus about one month for conventional carbon anodes)
- Improved circulation of electrolyte and separation of chlorine and aluminum product

Block Diagram or Photo:

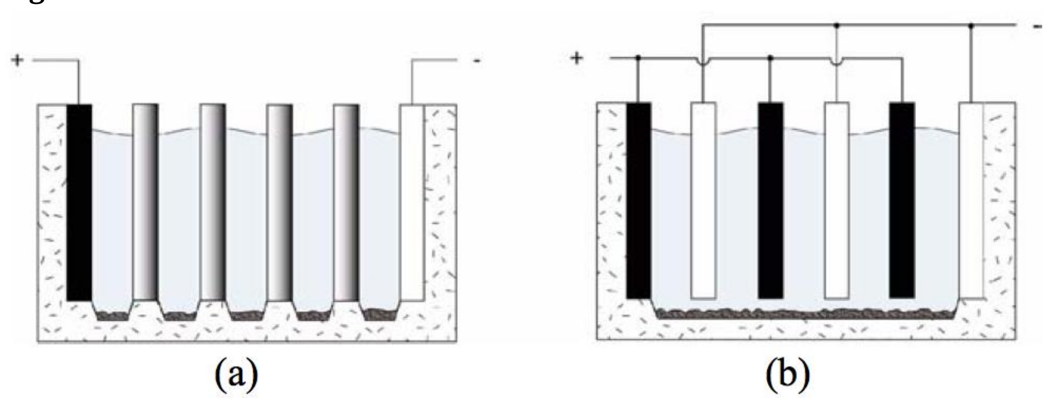


Figure 6. Multipolar cell with bipolar electrodes (a) between an anode (black) and cathode (white); multipolar cell with multiple anode and cathode pairs (b) (cell (Source: U.S. DOE 2007)

Commercial Status: Research and development stage

References for further information: U.S. DOE 2007

3.1.4. Novel Physical Designs for Anodes

Description:

Research on improving anodes used for Hall-Héroult aluminum smelting has largely focused on material choices. However, new physical designs for anodes can also improve energy efficiency and complement inert materials. Anode effects in a Hall-Héroult cell can be triggered by the formation of gaseous byproduct bubbles under the horizontal anode (Osarinmwian et al. 2014). The design of anodes in aluminum production cells can be altered to reduce anode effects and even promote a closer anode-cathode distance, which lowers energy requirements. Several anode designs have been recently commercialized. Sloped anodes and perforated or "slotted" anodes allow gaseous byproduct bubbles to safely circulate in the molten cryolite bath (Zhou et al. 2007). These designs also allow the cryolite bath to circulate more quickly, making the electrolysis of alumina more efficient.

In addition to novel anode shapes, vertical electrode cells are a complementary design for the various electrode technologies described above. Vertical electrode cells feature a vertically-oriented anode that also improves electrical conductivity by allowing gaseous bubbles to escape more easily, thus reducing anode effects (Hryn et al. 2014). Vertical cells reduce the anode current density and cell voltage, saving energy, and they also reduce heat loss.

For certain designs, however, there are physical limitations that need improvement. Grinding and shaping carbon anode blocks makes the anodes susceptible to breakage during transport or manufacturing. Anode sawing is expensive due to equipment, energy, and disposal needs (Berlin et al. 2014).

Alcoa has already commercialized a simple slotted anode design, while Rio Tinto Alcan and Norsk Hydro have filed patents for upgraded anode designs and are testing them (Berlin et al. 2014).

Energy/Environment/Cost/Other Benefits:
Compared to conventional aluminum technologies, new anode designs could have the following benefits:

- Savings of 2 – 2.5 kWh of energy saved per kilogram of aluminum for slotted anode undersides (Osarinmwian et al. 2014)
- Can be easily combined with inert anode materials and/or wetted cathodes in retrofits or new-build cells for further energy and environmental benefits
- Vertical cell designs reduce the need for frequent adjustments of anode position in current cells to prevent anode effects, which can be operationally costly (Hryn et al. 2014)

Commercial Status: Commercial with low adoption (slotted anodes), research stage (vertical cells)

References for further information:
Osarinmwian et al. 2014, Zhou et al. 2007, Berlin et al. 2014, Hryn et al. 2014

3.2. Alternative Reduction Technologies

The subsections below describe the emerging technologies that would provide entirely new aluminum production pathways, rather than improving upon the Hall-Héroult process.

3.2.1. Carbothermic Reduction

Description:

Unlike the Hall-Héroult process, carbothermic reduction is a non-electrolytic reaction. Carbothermic reduction reacts alumina with carbon at high temperatures to form aluminum and carbon monoxide (with an intermediate carbide product). These high temperatures are achieved through a furnace with different chambers for each reaction phase. Although carbothermic reduction requires high temperatures, it is a more thermodynamically efficient chemical reaction per unit of energy input than electrolysis in a Hall-Héroult cell (White et al. 2012). Although the concept of carbothermic smelting has been around for at least 50 years, it has long been considered impractical due to the high temperatures (around 2100 °C) and complicated product capture techniques necessary for reduction (Balomenos 2011). However, recent technological developments have made carbothermic reduction more potentially achievable as a smelting technology that saves energy, among other benefits. In addition, carbothermic reduction can be carried out on a small to medium scale much more easily than Hall-Héroult process, indicating that it could easily integrate with mini-mills and other new, closed-loop, recycling-oriented smelter designs (discussed below). The high temperature required for carbothermic reduction can allow integration of a greater range of alumina qualities and even scrap metal (White et al. 2012).

A major design challenge for the carbothermic process is that the high heat at which the reaction takes place leads to the loss of aluminum vapors, since the reactants are in gaseous form at that temperature (White et al. 2012). But, at lower temperatures, various aluminum carbides form which lead to a decreased reaction efficiency. In addition, the final aluminum that is produced is a carbon-aluminum alloy that eventually needs to be separated, taking additional energy and resources (Balomenos 2011).

In 2011, Alcoa established the Alcoa Norway Carbothermic group, including a pilot reactor in southern Norway (White et al. 2012). Alcoa developed this technology, called the Advanced Reactor Process (ARP), with support from the U.S. Department of Energy. The ARP furnace addresses some of the challenges of carbothermic smelting – for example, it includes cooled off-gas pipes to divert the aluminum vapors. Alcoa has tested the pilot for several weeks at a time – the pilot is large enough such that it can produce several tons of aluminum (White et al. 2012).

A company called ENEXAL is experimenting with carbothermic reduction in a vacuum, using an improved electric arc furnace with dual condensation zones and an improved pellet bed design (Balomenos 2011). In addition, they are experimenting with concentrated solar energy to power the furnace, which can reduce overall CO_2 emissions and fossil fuel energy needs (Kruesi 2011) (Vishnevetsky et al. 2014).

Energy/Environment/Cost/Other Benefits:

Compared to conventional Hall-Héroult smelting, carbothermic reduction can have the following benefits:

- Reduces energy used per unit of aluminum produced by around 20-30% (White et al. 2012) (U.S. DOE 2000)
- Could reduce capital costs by 50% and lower operating costs significantly (Balomenos 2011) (U.S. DOE 2000)

Block Diagram or Photo:

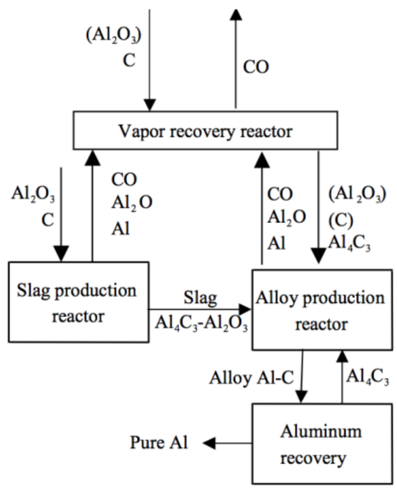


Figure 7. Flow chart of carbothermic aluminum production. Source: U.S. DOE 2000

Commercial Status*:* Pilot stage

References for further information:

U.S. DOE (2000), Balomenos (2011), White et al. (2012), Kruesi (2011), Vishnevetsky et al. (2014)

3.2.2. Kaolinite Reduction

Description:

Kaolinite reduction is an alternative to both the Bayer process for producing alumina and the Hall-Héroult smelting process. Kaolin is a common clay mineral formed from silicon oxides and aluminum oxides. Kaolinite reduction processes kaolin clay in a similar manner to bauxite, producing a dehydrated, calcined clay. This clay is then carbo-chlorinated in a reaction with clay oxides and coke, forming aluminum chloride. The aluminum chloride is then electrolyzed to aluminum and chlorine gas in a smelting cell. Aluminum chloride reduction cells are multipolar, using multiple stacked bipolar graphite electrodes, separated by inert spacers, in a chloride bath. In addition to operating at a lower temperature, such cells would have a lower volume than Hall-Héroult cells, allowing them to retain temperature more efficiently.

Production of pure aluminum from kaolin clay and aluminum chloride actually predates the Hall-Héroult process, but it never achieved commercialization due to ore purity issues and high costs.

Energy/Environment/Cost/Other Benefits:

Compared to the current Bayer and Hall-Héroult processes, the chlorination and reduction of kaolin clay could have the following benefits:

- A new source of widely available and inexpensive ore
- Faster and more efficient conversion in aluminum chloride production and reduction reactions, allowing less electricity to be used and overall energy savings of 12% - 46% (U.S. DOE 2007)
- Smaller cells with the ability to retain temperature and idle would allow aluminum producers to take advantage of electricity demand response systems, saving money on energy

Block Diagram or Photo:

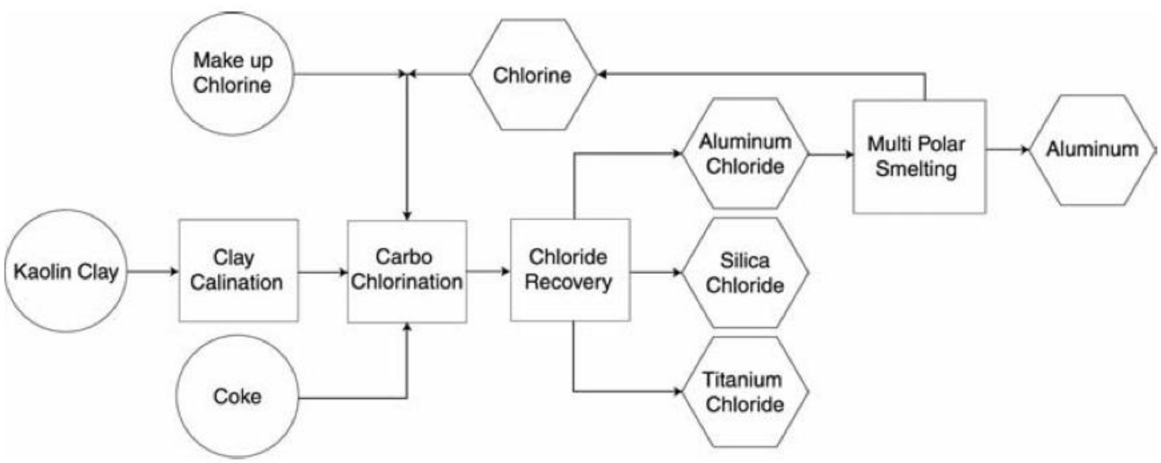


Figure 8. Process schematic of kaolin clay to aluminum. Source: U.S. DOE 2007

Commercial Status*:* Research stage

References for further information:

U.S. DOE (2007)

3.3. Low-Temperature Reduction

Although the majority of energy used in the Hall-Héroult process is consumed in the form of electricity for the electrolysis process, maintaining the high temperature of the cells is another major form of on-site energy use. Lowering the temperature at which smelting takes place can significantly reduce energy use and costs.

3.3.1. Ionic Liquids

Description

Currently, the smelting of aluminum uses molten aluminum fluoride-sodium bath as the electrolyte in which alumina is dissolved. In order to keep the bath in liquid phase, very high temperatures (900 – 1,000 °C) must be maintained, which is highly energy-intensive. Ionic liquids, which refer to a range of non-conventional organic solvents, electrolytes, and molten salts that have a low melting temperature, could dramatically reduce the necessary smelting temperature for aluminum (Zhang et al. 2003). Ionic liquids could replace the bath in which Hall-Héroult electrolysis currently occurs, allowing electrolysis to take place at close to room temperature. Several classes of ionic liquids have been studied, including chloroaluminate molten salts, fluoromethane salts, and imidazolium sulfate compounds (Markiewicz et al. 2009) (Poulimenou et al. 2015).

Ionic liquids can also be used in other phases of the aluminum production cycle. They can be used without being depleted to electro-refine aluminum scrap to make aluminum recycling more efficient (R. G. Reddy 2007). This process can also be used to electro-refine aluminum alloy to a more pure form.

Ionic liquids are very expensive, and some of the molten salts are highly water-attracting and difficult to purify (Zhang et al. 2003). In addition, they are less conductive than the current baths (Markiewicz et al. 2009). For these reasons, ionic liquids could be more suitable for electroplating products with aluminum rather than producing large quantities of primary aluminum. After several U.S. Department of Energy-supported studies in the early 2000s on ionic liquids for primary aluminum production, recent research has focused on smaller-scale electroplating applications with novel ionic liquid chemistries (Rocher et al. 2009).

Energy/Environment/Cost/Other Benefits:

Compared to conventional aluminum technologies, ionic liquids could have the following benefits:

- Save 30%-85% of energy compared to Hall-Héroult smelting, due to low-temperature reaction (Zhang et al. 2003) (Reddy 2007)
- Reduce polluting gases, like carbon monoxide, and solid wastes from spent linings in current Hall-Héroult cells (Zhang et al. 2003).
- Increase efficiency of bauxite-to-alumina conversion (Poulimenou et al. 2015).

Commercial Status: Research and development

References for further information: Zhang et al. (2003), Markiewicz et al. (2009), Poulimenous et al. (2015), Reddy (2007), Rocher et al. (2009)

3.4. Carbon Capture and Storage Technologies for the Aluminum Industry

While using low-carbon electricity sources for Hall-Héroult electrolysis could abate much of the carbon dioxide produced by aluminum smelting, the reaction of alumina with carbon-based anodes necessarily produces CO_2 as a reaction product. Carbon capture and storage (CCS) can significantly reduce the on-site carbon emissions from primary aluminum production.

3.4.1. Carbon Capture Using Absorption Technologies

Description:
A number of materials have been studied for capturing the CO_2 evolved from Hall-Héroult electrolysis through absorption. These absorbents include monoethanolamine (MEA) and ammonia. Absorbent-based carbon capture is a relatively well-characterized technology for major point sources of carbon emissions such a power plants, but has yet to be applied to an aluminum plant. Current design proposals would retrofit a Hall-Héroult cell by inserting a gas collector system to capture concentrated CO_2 (Jilvero et al. 2014). This system would allow flue gas to flow past the absorbent, producing a CO_2-rich liquid. The CO_2 would then be separated from the liquid in a heat exchanger that could use excess heat from the cells to re-form the absorbent. The CO_2 would be condensed into a liquid for storage.

One challenge for absorbent-based CCS within Hall-Héroult cells is maintaining a high CO_2 concentration in the flue gas. Currently, flue gas coming out of Hall-Héroult cells is diluted with cooling air, leading to a CO_2 concentration of 0.6%, which is too low to effectively absorb the CO_2 (Jilvero et al. 2014). The design proposed above would expose the absorbent to flue gas with a CO_2 concentration of 4% or higher. Achieving higher concentrations would be more efficient in capturing carbon, but would also be very costly, as it would require complete replacement of cells. Another challenge is the degradation of absorbents. MEA in particular degrades over time due to contamination, heat, and oxidation (Jilvero et al. 2014). Ammonia is a promising alternative, but is relatively less-studied. In addition, without a source of market demand for liquefied CO_2 CCS retrofitting could cost over $100 per ton of CO_2 (Lassagne et al. 2013). Finally, an additional energy source would be needed to capture the CO_2. These costs and energy requirements could be lowered by using waste heat (Jilvero et al. 2014).

A number of studies have modeled potential absorbent systems in Hall-Héroult cells to estimate costs and optimal CO_2 concentrations, using Norwegian aluminum smelters as the modeling base (Jilvero et al. 2014) (Mathisen et al. 2014a) (Mathisen et al. 2014b). These studies have not yet piloted physical designs.

Energy/Environment/Cost/Other Benefits:
Retrofitting aluminum plants with absorbent-based CCS technology could have the following benefits:

- Reducing CO_2 emissions by up to 85% (Mathisen et al. 2014b)
- Capturing up to 65% of waste heat for the CCS process (Mathisen et al. 2014b)

Block Diagram or Photo:

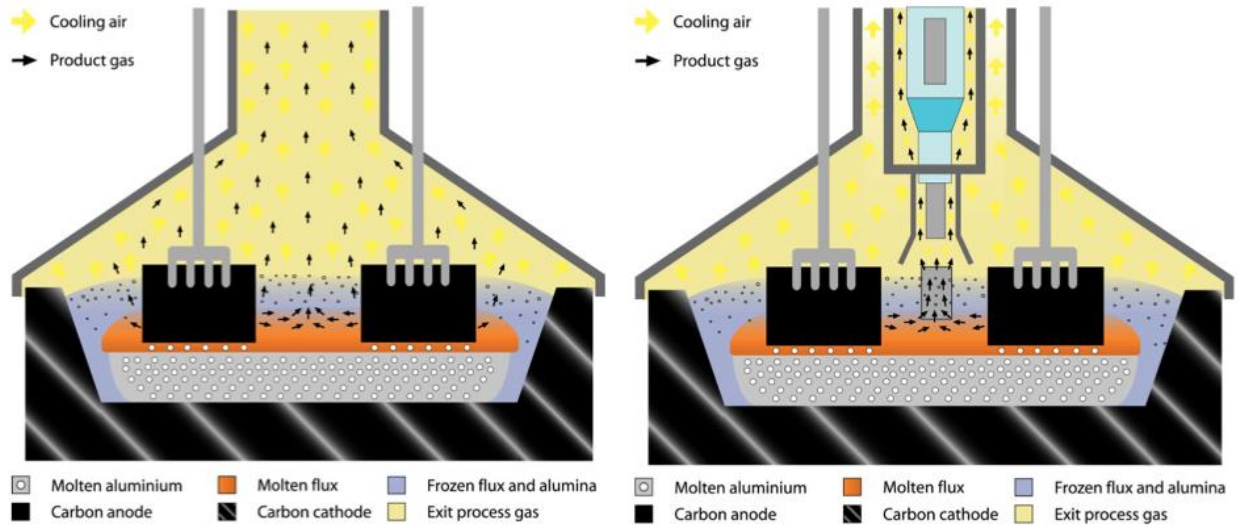


Figure 9. A current Hall-Heroult cell (left) and one with a potential CO_2 absorbent system (right) (Source: Jilvero et al. 2014)

Commercial Status*:* Research and Development stage

References for further information: Jilvero et al. (2014), Lassagne et al. (2013), Mathisen et al. (2014a), Mathisen et al. (2014b)

3.5. Emerging Aluminum Recycling Technologies

Aluminum recycling has possibly the largest energy-saving potential for the aluminum production process. Producing secondary aluminum from recycled sources consumes about 6 percent of the energy required to produce primary aluminum (U.S. DOE 2003). In the United States, about half of aluminum is produced from secondary sources, though this fraction is much lower for some other major aluminum producing countries (e.g. 20% from secondary sources in China). Advancing aluminum recycling techniques and improving the quality of secondary aluminum can save significant energy on a large scale.

3.5.1. Novel Physical Recycling Techniques

Description:

Physical sorting is necessary for isolating high-quality scrap metal in the secondary aluminum production process. Physically sorting scrap metal is almost always more economical than melt refining technology (Daley et al. 2013). Several novel physical recycling techniques can improve the quality of secondary aluminum. First, fluidized bed sink float technology is a technique that forces airflow over a bed of sand, controlling the density of the sand such that different density scraps can be separated. This also avoids the use of different chemical baths that are usually used for density sorting (Bell et al. 2003). Second, color sorting can be used to separate scrap aluminum by alloy type, eliminating many of the problems with mixing-based separation. Scraps are colored by an etching solution, then sorted by a computer trained on a certain color range (Gaustad et al. 2012). Finally, laser induced breakdown spectroscopy (LIBS) uses lasers to induce atomic emissions from the surface of scrap metal, which are read by detectors in the LIBS system. The system can then mechanically sort pieces of scrap. LIBS has the potential to be a high speed, high volume physical sorting technology with high specificity (Gaustad et al. 2012).

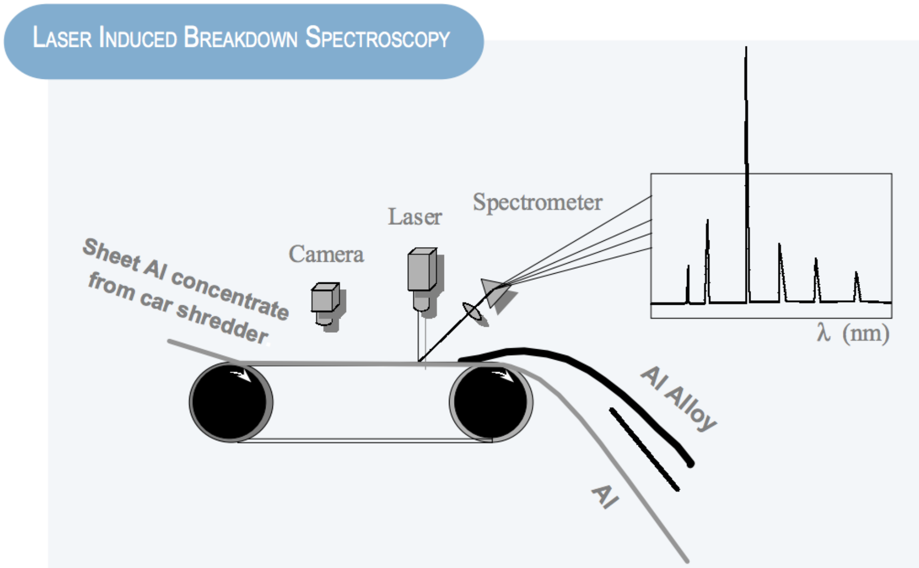
These techniques do have some limitations. For fluidized bed sink float technology, there are still issues with control and lubricant contamination on the scraps (Gaustad et al. 2012). Color sorting has a heavy environmental impact due to the use of etching chemicals, and still has issues with identification due to imperfections in the scrap metal. LIBS also works best with relatively unaltered scrap, which is a problem because much recycled aluminum has alloying agents such as magnesium, lubricants, paints, or other coatings (Gaustad et al. 2012).

In 1993, Alcan piloted a LIBS system (Daley et al. 2013), and later built a full-scale pilot plant to sort alloy with LIBS, where research is still being done (Green 2007). The Huron Valley Steel Company has used color sorting for aluminum scrap from the auto industry to group alloy families (U.S. DOE 2001).

Energy/Environment/Cost/Other Benefits:

- Secondary aluminum production energy savings of over 12% above and beyond current secondary production techniques (ACEEE 2015)
- Potential life cycle cost savings due to improved quality of secondary aluminum and energy cost savings

Block Diagram or Photo:



Alloy Sorting by Laser Induced Breakdown Spectroscopy (LIBS).

Figure 10: LIBS technology (U.S. DOE 2001)

Commercial Status: Demonstration stage

References for further information:
U.S. DOE (2001), Daley et al. (2013), Bell et al. (2003), Gaustad (2012), Green (2007), ACEEE (2015)

3.5.2. Aluminum Mini Mills

Description:
The novel physical scrap sorting techniques discussed earlier are necessary for further improvement of the aluminum recycling process. The development of highly efficient 'mini mills', which are small-scale mills that convert aluminum scrap directly into cast products, would be a major step for aluminum recycling and aluminum production. In the steel industry, mini mills that were able to utilize steel scrap were developed in the 1960s, transforming the steel production landscape by significantly lowering production costs (Apelian et al. 2014). The advancement of scrap sorting and melting technologies in the aluminum recycling industry could enable the spread of aluminum mini mills.

Mini mills use advanced scrap sorting technologies in order to generate a single, high quality melt of recycled aluminum, which is then cast or rolled within the mill. Mini mills reduce energy use through two mechanisms – first, by reducing the need for primary aluminum by using scrap metal, and second, by using aluminum scrap more efficiently. Mini mills eliminate several expensive and energy-intensive re-heating and cooling steps. Currently, most secondary aluminum is produced in ingots that are then shipped to rolling mills to be made into final products (Demeester. et al 2013). Unlike primary smelters or even large-scale secondary operations, mini mills don't need to be located in areas where low-cost electricity and energy are abundant – given their small scale, they can be located in more efficient manufacturing centers or close to where scrap is produced, reducing transportation-related energy and costs.

Mini mills face structural barriers within the aluminum industry. While primary aluminum production is highly integrated, with raw materials of bauxite or alumina often processed near to smelters, the secondary aluminum industry is more decentralized, with low-capital, high-labor operations spread out around the world (Buffington 2012). Mini mills will require significant up-front investment and planning transitions on the part of large aluminum producers before they can be scaled up.

In 2014, the U.S. Department of Energy's ARPA-E program funded the Center for Resource Recovery and Recycling at the Worcester Polytechnic Institute and several other partners to develop an Aluminum Integrated Minimill (AIM), including plans for pilot trials and commercial scaling (Apelian et al. 2014). Also in 2014, the company American Specialty Alloys announced plans to build an aluminum mini mill to convert recycled aluminum into automotive industry products.

Energy/Environment/Cost/Other Benefits:

- Allowing utilization of scrap aluminum close to its source. For example, in the United States, aluminum scrap is often shipped to China and India for manual sorting. The development of domestic mini mills would reduce the need to offshore scrap resources and sorting-related jobs.
- 84% lower energy needs than current scrap-to-product recycling techniques (Apelian et al. 2014).
- Could reduce industry-wide carbon emissions by 2.7 million tons/year (Apelian et al. 2014).
- In the United States alone, could save aluminum recyclers $1.1 billion per year through energy and material savings (Apelian et al. 2014).

Block Diagram or Photo:

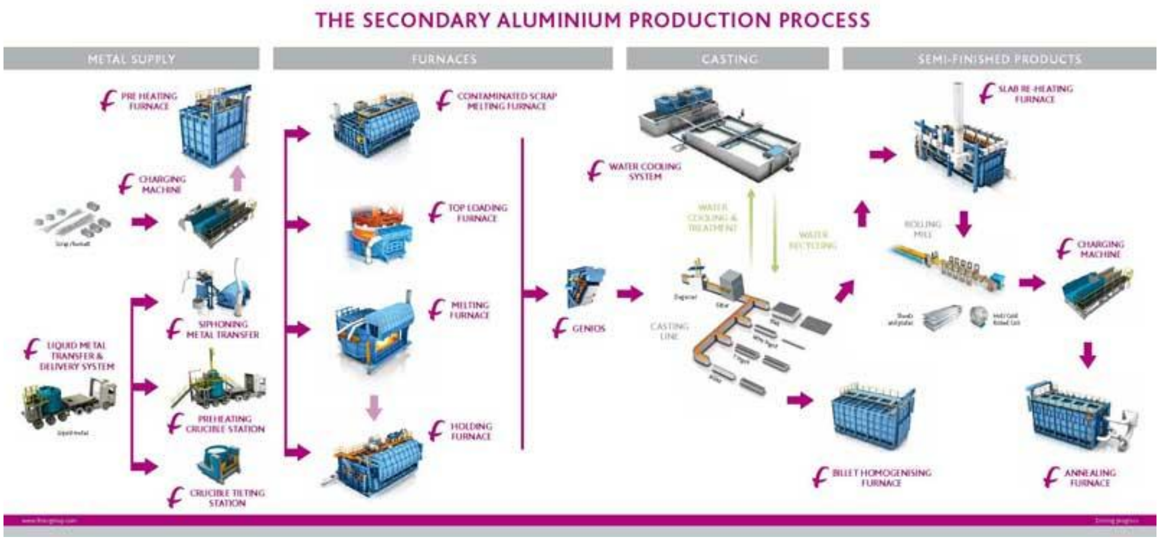


Figure 11: In a mini mill, all these processes would occur in the same mill. Source: Fives Group

Commercial Status*:* Pilot stage

References for further information:
Apelian et al. (2014), Demeester et al. (2013), Buffington (2012)

4. Conclusion

This paper describes 10 alternative emerging energy efficiency and CO_2 emissions reduction technologies or processes for the aluminum industry. The information presented for each technology was collected from various publicly available sources. It is likely that no single technology will be the best or only solution for a more energy efficient aluminum industry – instead, a portfolio of commercial and emerging technologies should be deployed to address the increasing energy use and CO_2 emissions of the aluminum industry.

As can be seen from the information presented in this paper, most of the technologies have not been commercialized yet. Therefore, further research is needed to improve and optimize these technologies in order to make them commercial. In addition, this catalogue focused on technologies for which there were multiple sources of information, thus excluding some promising emerging technologies that only had information available from the technology developer, for example. Conducting independent studies and validation on the fundamentals, development, and operation of these emerging technologies can be helpful to private and public sectors as well as academia.

Shifting away from conventional processes and products will require a number of developments including: education of producers and consumers; new standards; aggressive research and development to address the issues and barriers confronting emerging technologies; government support and funding for development and deployment of emerging technologies; rules to address the intellectual property issues related to dissemination of new technologies; and financial incentives (e.g., through carbon trading mechanisms) to make emerging low-carbon technologies, which might have higher initial costs, competitive with conventional processes and products. It should be noted that the purpose of this paper is solely informational.

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